



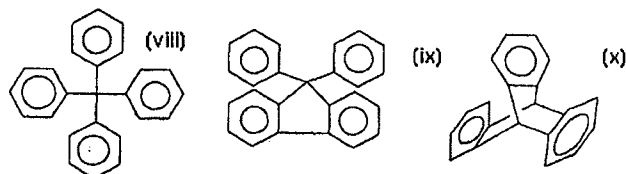
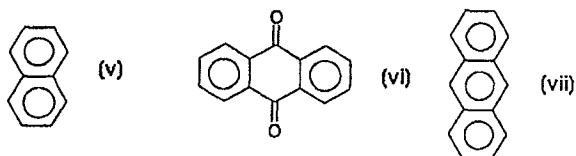
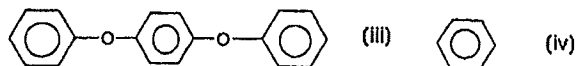
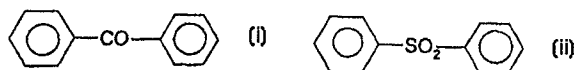
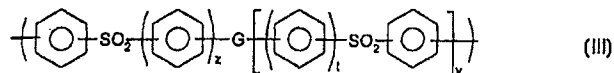
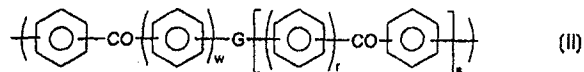
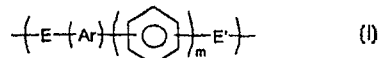
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| (21) International Application Number: PCT/GB99/02833 (22) International Filing Date: 10 September 1999 (10.09.99) (30) Priority Data: <table border="0"> <tr> <td>9819706.4</td> <td>11 September 1998 (11.09.98)</td> <td>GB</td> </tr> <tr> <td>9820940.6</td> <td>28 September 1998 (28.09.98)</td> <td>GB</td> </tr> <tr> <td>9913572.5</td> <td>11 June 1999 (11.06.99)</td> <td>GB</td> </tr> </table> (71) Applicant (for all designated States except US): VICTREX MANUFACTURING LIMITED [GB/GB]; Victrex Technology Centre, Hillhouse International, P.O. Box 4, Thornton Cleveleys, Lancashire FY5 4QD (GB). (72) Inventors; and (73) Inventors/Applicants (for US only): CHARNOCK, Peter [GB/GB]; 7 Elvaston Road, Carleton, Poulton-Le-Fylde, Lancashire FY6 7TH (GB). KEMMISH, David, John [GB/GB]; 10 Whittle Green, Woodplumpton, Preston, Lancashire PR4 0WG (GB). STANILAND, Philip, Anthony [GB/GB]; 3 Foster Street, Broughton, Saltburn by the Sea, Cleveland TS12 2TR (GB). WILSON, Brian [GB/GB]; 1 White Lea, Cabus, Garstang, Lancashire PR3 1JG (GB). (74) Agents: BRIERLEY, Anthony, Paul et al.; Appleyard Lees, 15 Clare Road, Halifax HX1 2HY (GB). | | 9819706.4 | 11 September 1998 (11.09.98) | GB | 9820940.6 | 28 September 1998 (28.09.98) | GB | 9913572.5 | 11 June 1999 (11.06.99) | GB | (81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments. | |
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(54) Title: ION-EXCHANGE POLYMERS

(57) Abstract

Ion-Exchange polymers for a polymer electrolyte membrane include a moiety of formula (I), and/or a moiety of formula (II), and/or a moiety of formula (III) wherein at least some of the units I, II and/or III are sulphonated; wherein the phenyl moieties in units I, II, and III are independently optionally substituted and optionally cross-linked; and wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from one of the above moieties (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties.



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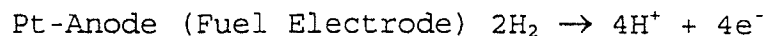
ION-EXCHANGE POLYMERS

This invention relates to ion-exchange polymers and particularly, although not exclusively, relates to
5 sulphonated polymers, for example sulphonated polyaryletherketones, polyarylethersulphones and/or copolymers of the aforesaid. Preferred embodiments of the invention relate to ion-conductive membranes, for example of polymer electrolyte membrane fuel cells, made using such
10 polymers. The invention also relates to novel non-sulphonated polyaryletherketones and/or polyarylethersulphones used for preparing said sulphonated polymers and processes for the preparation of polymers described herein.

15

A polymer electrolyte membrane fuel cell (PEMFC), shown schematically in Figure 1 of the accompanying diagrammatic drawings, may comprise a thin sheet 2 of a hydrogen-ion conducting Polymer Electrolyte Membrane (PEM) sandwiched on
20 both sides by a layer 4 of platinum catalyst and an electrode 6. The layers 2, 4, 6 make up a Membrane Electrode Assembly (MEA) of less than 1mm thickness.

In a PEMFC, hydrogen is introduced at the anode (fuel
25 electrode) which results in the following electrochemical reaction:



30 The hydrogen ions migrate through the conducting PEM to the cathode. Simultaneously, an oxidant is introduced at the cathode (oxidant electrode) where the following electrochemical reaction takes place:

Pt-Cathode (Oxidant Electrode) $O_2 + 4H^+ = 4e^- \rightarrow 2H_2O$

Thus, electrons and protons are consumed to produce
5 water and heat. Connecting the two electrodes through an
external circuit causes an electrical current to flow in
the circuit and withdraw electrical power from the cell.

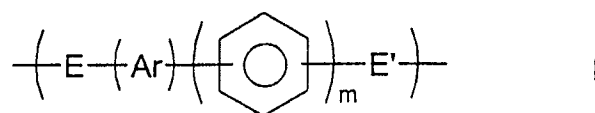
US Patent No. 5 561 202 (Hoechst) discloses the
10 production of PEMs from sulphonated aromatic polyether
ketones. At least 5% of the sulphonic groups in the
sulphonic acid moieties are converted into sulphonyl
chloride groups and then reacted with an amine containing
at least one cross-linkable substituent or a further
15 functional group. An aromatic sulphonamide is then
isolated, dissolved in an organic solvent, converted into a
film and then the cross-linkable substituents in the film
are cross-linked. The invention is said to provide ion-
conductive membranes suitable for use as polymeric solid
20 electrolytes which have adequate chemical stability and can
be produced from polymers which are soluble in suitable
solvents.

One problem associated with known PEMFCs is that of
25 providing PEMs which have desirable properties at elevated
temperatures and which are cheap to manufacture.

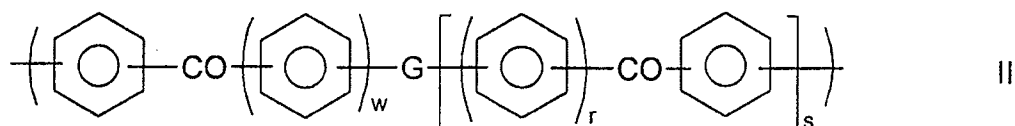
It is an object of the present invention to address
problems associated with PEMs.

30

According to a first aspect of the invention, there is
provided a polymer electrolyte membrane which includes a
polymer having a moiety of formula

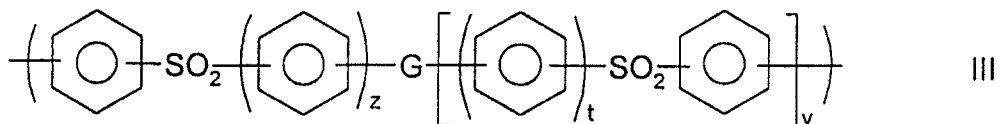


and/or a moiety of formula

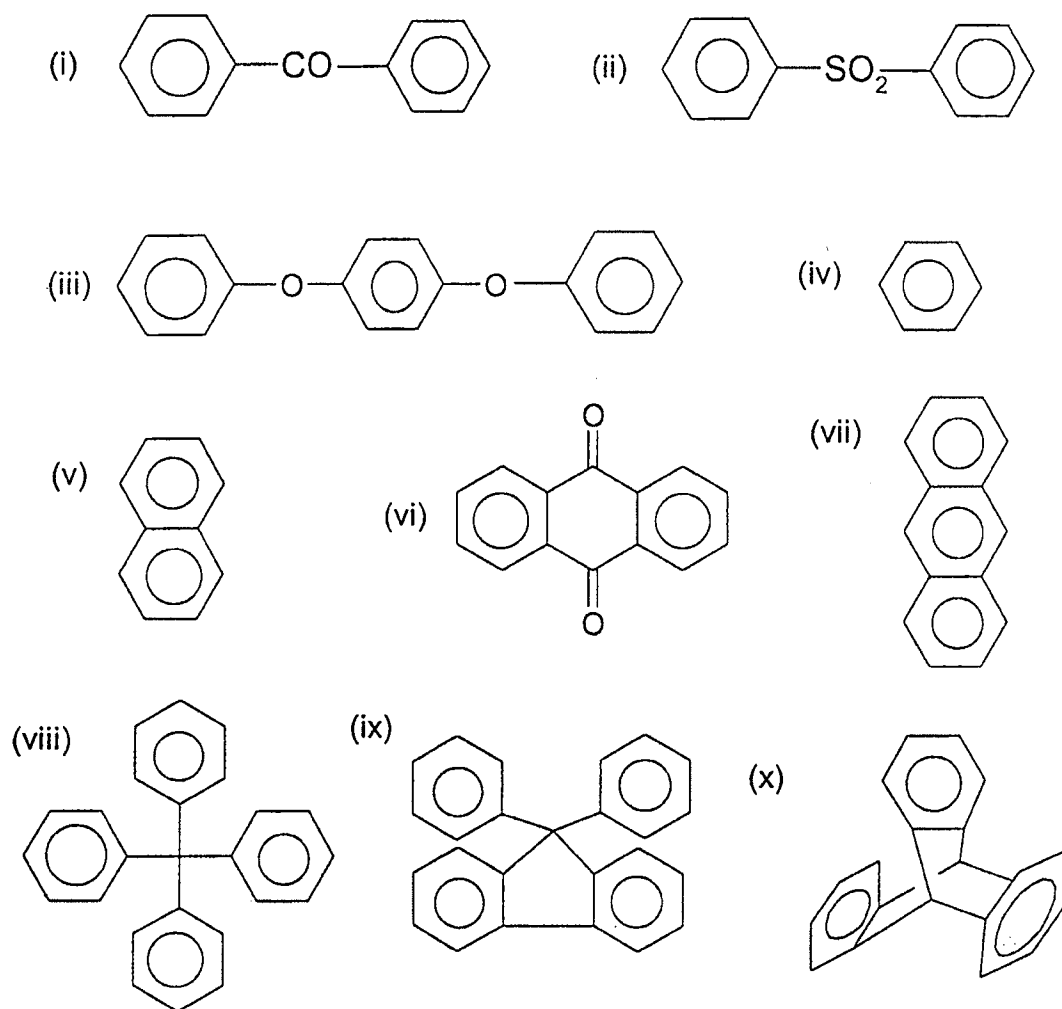


5

and/or a moiety of formula



wherein at least some of the units I, II and/or III are
 10 sulphonated; wherein the phenyl moieties in units I, II,
 and III are independently optionally substituted and
 optionally cross-linked; and wherein m, r, s, t, v, w and z
 independently represent zero or a positive integer, E and
 E' independently represent an oxygen or a sulphur atom or a
 15 direct link, G represents an oxygen or sulphur atom, a
 direct link or a -O-Ph-O- moiety where Ph represents a
 phenyl group and Ar is selected from one of the following
 moieties (i) to (x) which is bonded via one or more of its
 phenyl moieties to adjacent moieties



The invention extends to a polymer electrolyte membrane which includes a polymer having a moiety of formula I and/or a moiety of formula II and/or a moiety of formula III as described according to said first aspect, wherein at least some of units I, II and/or III are functionalised to provide ion exchange sites. Suitably, to provide said ion exchange sites, said polymer is sulphonated, phosphorylated, carboxylated, quaternary-aminoalkylated or chloromethylated, and optionally further modified to yield -CH₂PO₃H₂, -CH₂NR₃²⁰⁺ where R²⁰ is an alkyl, or -CH₂NAr₃^{x+} where Ar^x is an aromatic (arene), to provide a cation or anion exchange membrane. Further still, the aromatic moiety may

contain a hydroxyl group which can be readily elaborated by existing methods to generate $-\text{OSO}_3\text{H}$ and $-\text{OPO}_3\text{H}_2$ cationic exchange sites on the polymer. Ion exchange sites of the type stated may be provided as described in WO95/08581.

5

References to sulphonation include a reference to substitution with a group $-\text{SO}_3\text{M}$ wherein M stands for one or more elements selected with due consideration to ionic valencies from the following group: H, NR_4^{Y+} , in which R^Y stands for H, $\text{C}_1\text{-C}_4$ alkyl, or an alkali or alkaline earth metal or a metal of sub-group 8, preferably H, NR_4^+ , Na, K, Ca, Mg, Fe, and Pt. Preferably M represents H. Sulphonation of the type stated may be provided as described in WO96/29360.

15

Unless otherwise stated in this specification, a phenyl moiety may have 1,4- or 1,3-, especially 1,4-, linkages to moieties to which it is bonded.

20 Said polymer may include more than one different type of repeat unit of formula I; more than one different type of repeat unit of formula II; and more than one different type of repeat unit of formula III.

25 Said moieties I, II and III are suitably repeat units. In the polymer, units I, II and/or III are suitably bonded to one another - that is, with no other atoms or groups being bonded between units I, II, and III.

30 Where the phenyl moieties in units I, II or III are optionally substituted, they may be optionally substituted by one or more halogen, especially fluorine and chlorine, atoms or alkyl, cycloalkyl or phenyl groups. Preferred

alkyl groups are C₁₋₁₀, especially C₁₋₄, alkyl groups. Preferred cycloalkyl groups include cyclohexyl and multicyclic groups, for example adamantyl. In some cases, the optional substituents may be used in the cross-linking
5 of the polymer. For example, hydrocarbon optional substituents may be functionalised, for example sulphonated, to allow a cross-linking reaction to take place. Preferably, said phenyl moieties are unsubstituted.

10 Another group of optional substituents of the phenyl moieties in units I, II or III include alkyls, halogens, C_yF_{2y+1} where y is an integer greater than zero, O-R^q (where R^q is selected from the group consisting of alkyls, perfluoralkyls and aryls), CF=CF₂, CN, NO₂ and OH.
15 Trifluormethylated phenyl moieties may be preferred in some circumstances.

Where said polymer is cross-linked, it is suitably cross-linked so as to improve its properties as a polymer
20 electrolyte membrane, for example to reduce its swellability in water. Any suitable means may be used to effect cross-linking. For example, where E represents a sulphur atom, cross-linking between polymer chains may be effected via sulphur atoms on respective chains.
25 Alternatively, said polymer may be cross-linked via sulphonamide bridges as described in US 5 561 202. A further alternative is to effect cross-linking as described in EP-A-0008895.

30 However, for polymers according to the first aspect or second aspect which are crystalline (which some are) there may be no need to effect cross-linking to produce a material which can be used as a polymer electrolyte

membrane. Such polymers may be easier to prepare than cross-linked polymers. Thus, said polymer of the first and/or second aspects may be crystalline. Preferably, said polymer is not optionally cross-linked as described.

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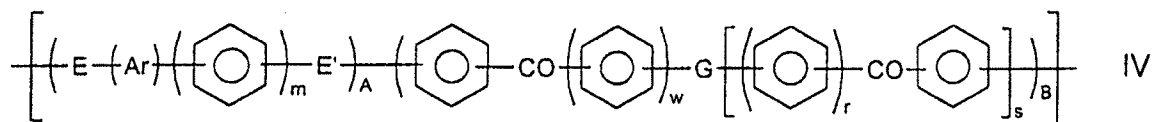
Where w and/or z is/are greater than zero, the respective phenylene moieties may independently have 1,4- or 1,3-linkages to the other moieties in the repeat units of formulae II and/or III. Preferably, said phenylene
10 moieties have 1,4- linkages.

Preferably, the polymeric chain of the polymer does not include a -S- moiety. Preferably, G represents a direct link.

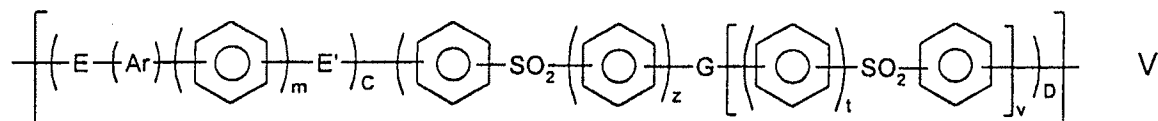
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Suitably, "a" represents the mole % of units of formula I in said polymer, suitably wherein each unit I is the same; "b" represents the mole % of units of formula II in said polymer, suitably wherein each unit II is the same;
20 and "c" represents the mole % of units of formula III in said polymer, suitably wherein each unit III is the same. Preferably, a is in the range 45-100, more preferably in the range 45-55, especially in the range 48-52. Preferably, the sum of b and c is in the range 0-55, more
25 preferably in the range 45-55, especially in the range 48-52. Preferably, the ratio of a to the sum of b and c is in the range 0.9 to 1.1 and, more preferably, is about 1. Suitably, the sum of a, b and c is at least 90, preferably at least 95, more preferably at least 99, especially about
30 100. Preferably, said polymer consists essentially of moieties I, II and/or III.

Said polymer may be a homopolymer having a repeat unit of general formula



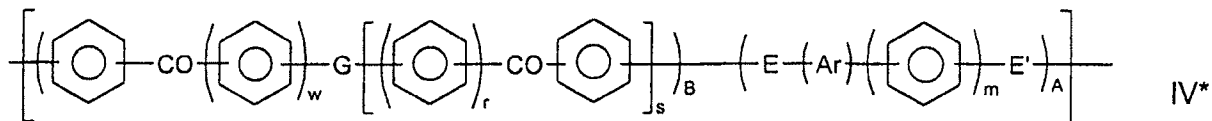
or a homopolymer having a repeat unit of general
5 formula



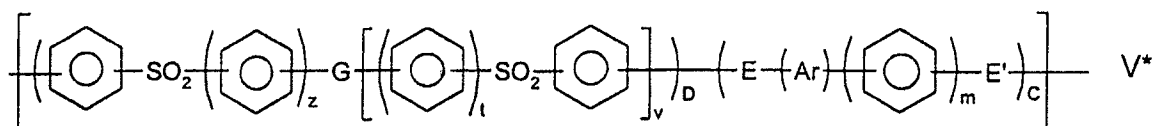
or a random or block copolymer of at least two different units of IV and/or V

10 wherein A, B, C and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

As an alternative to a polymer comprising units IV
15 and/or V discussed above, said polymer may be a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general
20 formula



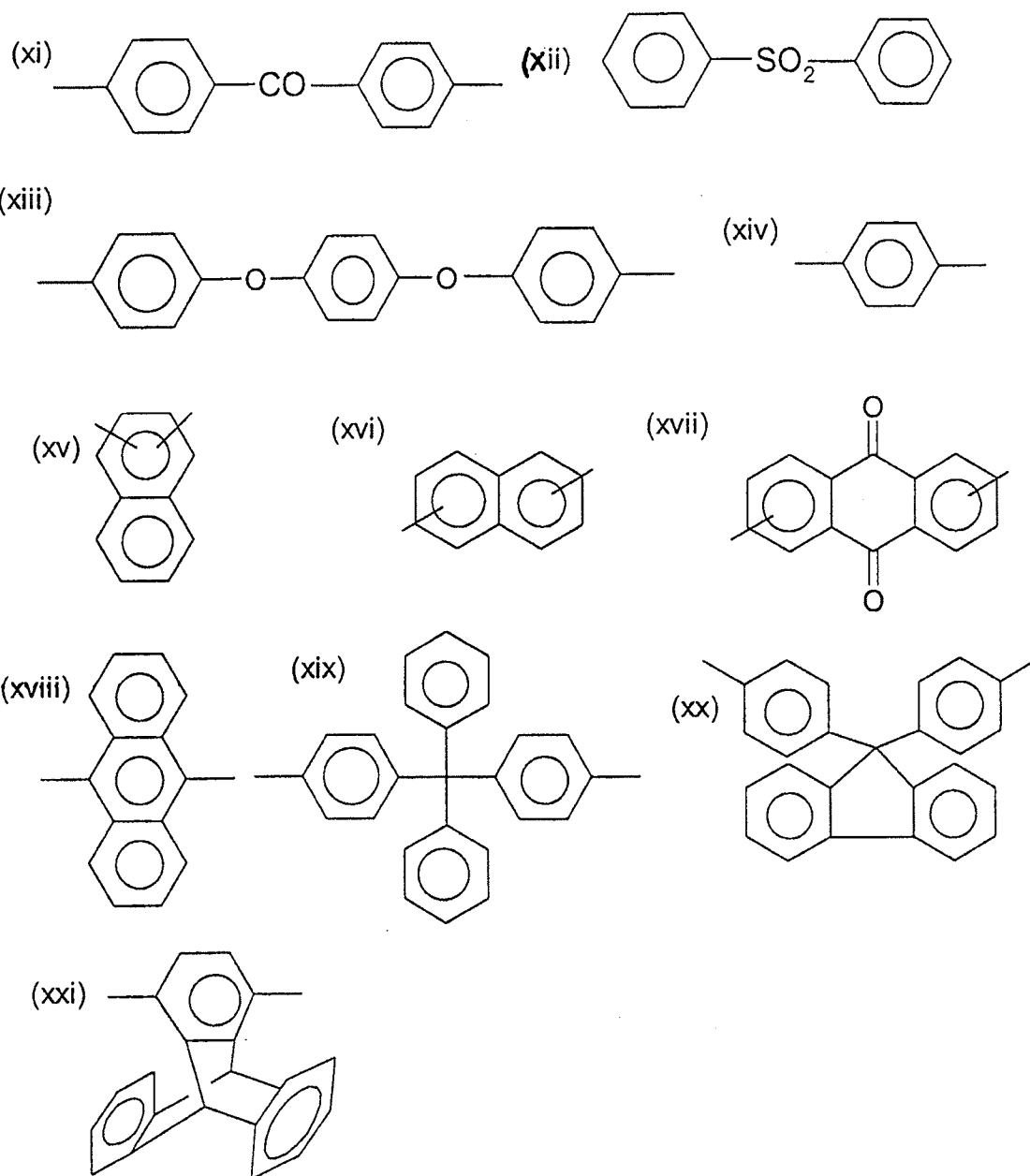
or a random or block copolymer of at least two different units of IV* and/or V*, wherein A, B, C, and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

5

Preferably, m is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, r is in the range 0-3, more preferably 0-2, especially 0-1. Preferably t is in the range 0-3, more preferably 0-2, especially 0-1.

10 Preferably, s is 0 or 1. Preferably v is 0 or 1. Preferably, w is 0 or 1. Preferably z is 0 or 1.

Preferably Ar is selected from the following moieties
(xi) to (xxi):



Preferably, (xv) is selected from a 1,2-, 1,3-, or a 1,5-moiety; (xvi) is selected from a 1,6-, 2,3-, 2,6- or a 2,7-moiety; and (xvii) is selected from a 1,2-, 1,4-, 1,5-, 1,8- or a 2,6- moiety.

5

One preferred class of polymers may include at least some ketone moieties in the polymeric chain. In such a preferred class, the polymer preferably does not only include -O- and -SO₂- moieties between aryl (or other
10 unsaturated) moieties in the polymeric chain. Thus, in this case, suitably, a polymer of the first and/or second aspects does not consist only of moieties of formula III, but also includes moieties of formula I and/or II.

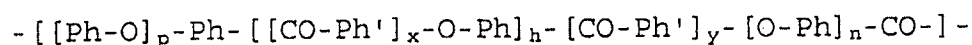
15 One preferred class of polymers does not include any moieties of formula III, but suitably only includes moieties of formulae I and/or II. Where said polymer is a homopolymer or random or block copolymer as described, said homopolymer or copolymer suitably includes a repeat unit of
20 general formula IV. Such a polymer may, in some embodiments, not include any repeat unit of general formula V.

Referring to formula IV, preferably, said polymer is
25 not a polymer wherein: Ar represents moiety (iv), E and E' represent oxygen atoms, m represents zero, w represents 1, s represents zero, and A and B represent 1; Ar represents moiety (i), E and E' represent oxygen atoms, G represents a direct link, m represents zero, w represents 1, r
30 represents 0, s represents 1 and A and B represent 1; Ar represents moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents 0, w represents 0, s represents 1, r represents 1 and A and B represent 1.

Referring to formula V, preferably Ar represents moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents zero, z represents 1, v represents zero and C and D represent 1.

5

Preferably, said polymer is not a sulphonated aromatic polyetherketone of formula

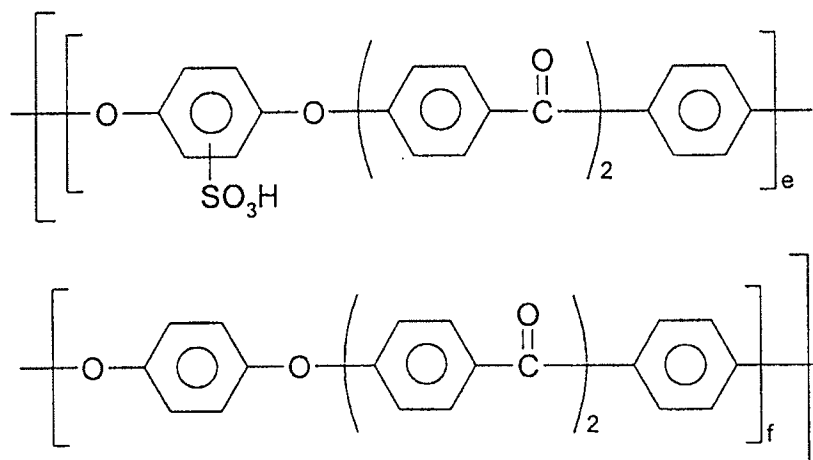


10

where Ph represents a 1,4- or 1,3- phenylene moiety; Ph' represents phenylene, naphthylene, biphenylene or anthrylene; p is 1, 2, 3 or 4; x, h and n are, independently, zero or 1; and y is 1, 2 or 3.

15

Preferably, said polymer does not conform to the formula



20

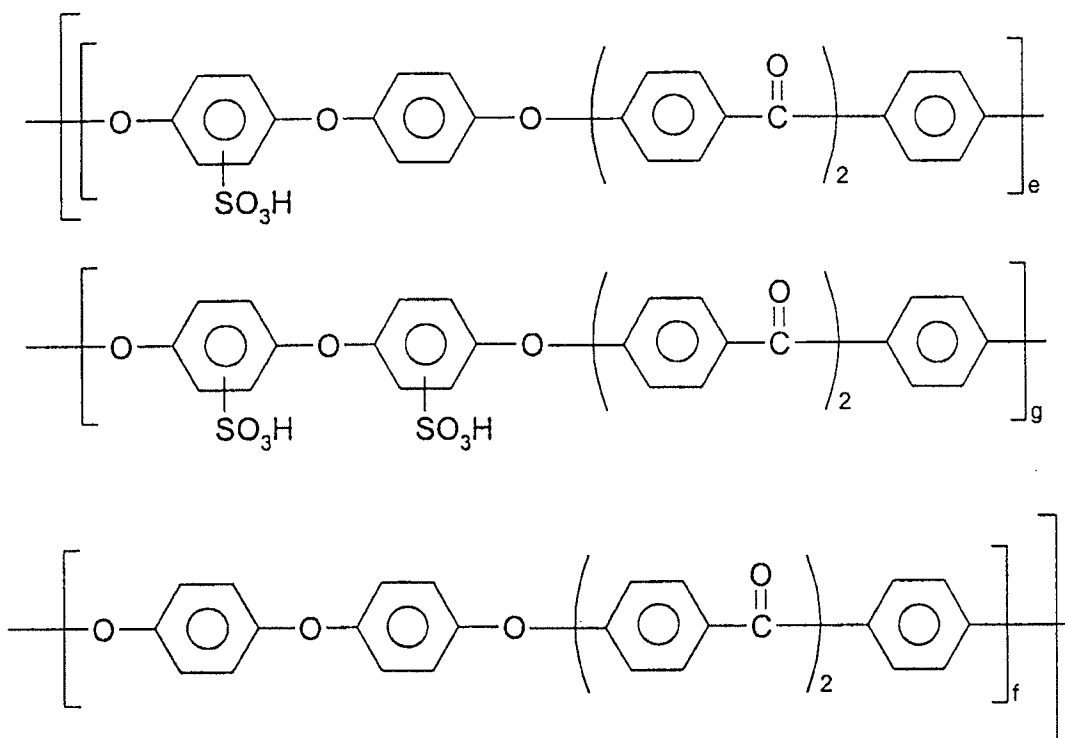
where

e is from 0.2 to 1,

f is from 0 to 0.8, and

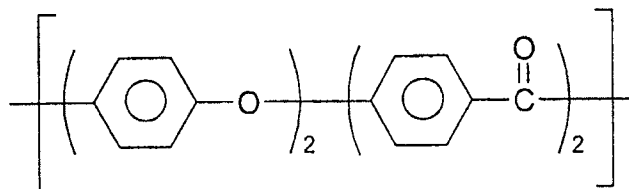
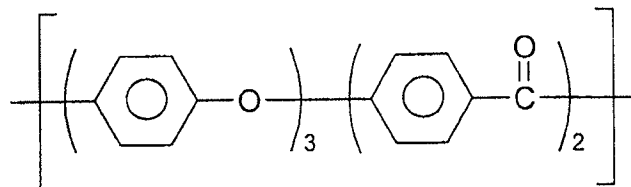
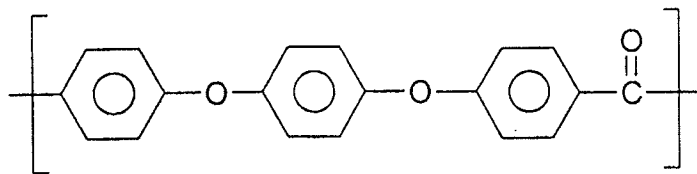
e + f = 1

Preferably, said polymer does not conform to the formula



5 in which e is a number from 0 to 1, g is a number from 0 to 1, f is a number from 0 to 0.5, and the sum $e + f + g = 1$.

Preferably, said polymer is not a copolymer built up
10 from at least two different units of formulae:



Suitable moieties Ar are moieties (i), (ii), (iv) and (v) and, of these, moieties (i), (ii) and (iv) are preferred. Preferred moieties Ar are moieties (xi), (xii), (xiv), (xv) and (xvi) and, of these, moieties (xi), (xii) and (xiv) are especially preferred. Another preferred moiety is moiety (v), especially, moiety (xvi). In relation, in particular to the alternative polymers comprising units IV* and/or V*, preferred Ar moieties are (v) and, especially, (xvi).

Preferred polymers include an electron-rich, relatively non-deactivated, easily sulphonatable unit, for example a multi-phenylene moiety or a fused-rings aromatic moiety, such as naphthalene. Such an easy to sulphonate unit may be sulphonated under relatively mild conditions to introduce two sulphonate groups per unit. Thus, preferred polymers may have at least 10 π electrons in a delocalized aromatic moiety. The number of π electrons may be 12 or less.

Preferred polymers include a biphenylene moiety. Other preferred polymers include a naphthalene moiety. Preferred polymers include said electron rich, non-deactivated, easily sulphonatable unit bonded to two oxygen atoms.

5 Especially preferred polymers include a -O-biphenylene-O-moiety. Other especially preferred polymers include a -O-naphthalene-O- moiety.

Preferred polymers include a first type of moiety which is relatively difficult to sulphonate and a second type of moiety which is relatively easy to sulphonate. For example, said second moiety may be sulphonatable using the relatively mild method described in Example 13 hereinafter, whereas the first moiety may be substantially non-sulphonatable in such a method. The use of the method of Example 13 may be advantageous over currently used methods which use oleum. A preferred second said moiety includes a moiety $-\text{Ph}_n-$ wherein n is an integer of at least 2. Said moiety is preferably bound to at least one ether oxygen.

10 is relatively difficult to sulphonate and a second type of moiety which is relatively easy to sulphonate. For example, said second moiety may be sulphonatable using the relatively mild method described in Example 13 hereinafter, whereas the first moiety may be substantially non-sulphonatable in such a method. The use of the method of Example 13 may be advantageous over currently used methods which use oleum. A preferred second said moiety includes a moiety $-\text{Ph}_n-$ wherein n is an integer of at least 2. Said moiety is preferably bound to at least one ether oxygen.

15 sulphonatable in such a method. The use of the method of Example 13 may be advantageous over currently used methods which use oleum. A preferred second said moiety includes a moiety $-\text{Ph}_n-$ wherein n is an integer of at least 2. Said moiety is preferably bound to at least one ether oxygen.

20 Especially preferred is the case wherein said moiety is -O- Ph_n -O- where said ether groups are para to the Ph-Ph bond.

Preferred polymers are copolymers comprising a first repeat unit which is selected from the following:

25 (a) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1;

30 (b) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety

of structure (i), m represents zero, A represents 1, B represents zero;

(c) a unit of formula V wherein E and E' represent
5 oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1 and C and D represent 1;

(d) a unit of formula V wherein E represents an oxygen
10 atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; or

(e) a unit of formula V wherein E and E' represents an
15 oxygen atom, Ar represents a structure (i), m represents 0, C represents 1, Z represents 1, G represents a direct link, v represents 0 and D represents 1;

and a second repeat unit which is selected from the
20 following:

(f) a unit of formula IV wherein E and E' represent
oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s
25 represents zero, A and B represent 1;

(g) a unit of formula IV wherein E represents an oxygen
atom, E' is a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent
30 zero, w represent 1, A and B represent 1;

(h) a unit of formula V wherein E and E' represent
oxygen atoms, G represents a direct link, Ar represents a

moiety of structure (iv), m represents 1, z represents 1, v represents 0, C and D represent 1; and

(i) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1, C and D represent 1;

Other second units which may form copolymers with any of said first repeat units (a) to (e) above include: a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, w represents 1, s represents 0, A and B represent 1; or a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, z represents 1, v represents 0, C and D represent 1.

Preferred polymers for some situations may comprise first units selected from (a), (b), (c) and (e) and second units selected from (f), (g), (h) or (i). A polymer comprising units (d) and (h) may also be preferred.

More preferred polymers are copolymers having a first repeat unit selected from those described above, especially repeat units (b), (d) or (e) in combination with a second repeat unit selected from units (f) or (h).

Preferred polymers having repeat unit(s) of formulae IV* and V* may include: a unit of formula IV* wherein Ar represents a moiety of structure (v), E represents a direct link, E' represents an oxygen atom, G represents a direct link, w, s and m represent 0, A and B represent 1; and/or a

repeat unit of formula V* wherein Ar represents a moiety of structure (v), E represents a direct link, E' represents an oxygen atom, G represents a direct link, z, v and m represent 0, C and D represent 1.

5

Said polymers having repeat units IV* and V* may include any of repeat units (a) to (i) described above.

In some situations, polymers which include at least one
10 repeat unit of formula IV or formula IV* may be preferred.

Copolymers may be prepared having one or more first repeat units and one or more of said second repeat units.

15 Where said polymer is a copolymer as described, the mole% of co-monomer units, for example said first and second repeat units described above, may be varied to vary the solubility of the polymer in solvents, for example in organic solvents which may be used in the preparation of
20 films and/or membranes from the polymers and/or in other solvents, especially water.

Preferred polymers suitably have a solubility of at least 10% w/v, preferably a solubility in the range 10 to
25 30 %w/v in a polar aprotic solvent, for example NMP, DMSO or DMF. Preferred polymers are substantially insoluble in boiling water.

First units of the type described above (with the
30 exception of units (a) and (c)) may be relatively difficult to sulphonate, whereas second units of the type described may be easier to sulphonate.

Where a phenyl moiety is sulphonated, it may only be mono-sulphonated. However, in some situations it may be possible to effect bi- or multi-sulphonation.

5 In general terms, where a said polymer includes a -O-phenyl-O- moiety, up to 100 mole% of the phenyl moieties may be sulphonated. Where a said polymer includes a -O-biphenylene-O- moiety, up to 100 mole% of the phenyl moieties may be sulphonated. It is believed to be possible
10 to sulphonate relatively easily -O-(phenyl)_n-O- moieties wherein n is an integer, suitably 1-3, at up to 100 mole%. Moieties of formula -O-(phenyl)_n-CO- or -O-(phenyl)_n-SO₂- may also be sulphonated at up to 100 mole% but more vigorous conditions may be required. Moieties of formulae
15 -CO-(phenyl)_n-CO- and -SO₂-(phenyl)_n-SO₂- are more difficult to sulphonate and may be sulphonated to a level less than 100 mole% or not at all under some sulphonation conditions.

The glass transition temperature (T_g) of said polymer
20 may be at least 144°C, suitably at least 150°C, preferably at least 154°C, more preferably at least 160°C, especially at least 164°C. In some cases, the T_g may be at least 170°C, or at least 190°C or greater than 250°C or even 300°C.

25

Said polymer may have an inherent viscosity (IV) of at least 0.1, suitably at least 0.3, preferably at least 0.4, more preferably at least 0.6, especially at least 0.7 (which corresponds to a reduced viscosity (RV) of least
30 0.8) wherein RV is measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84gcm⁻³, said solution containing 1g of polymer per 100cm⁻³ of solution. IV is measured at 25°C on a solution of polymer

in concentrated sulphuric acid of density 1.84gcm^3 , said solution containing 0.1g of polymer per 100cm^3 of solution.

The measurements of both RV and IV both suitably employ
5 a viscometer having a solvent flow time of approximately 2 minutes.

The main peak of the melting endotherm (T_m) for said polymer (if crystalline) may be at least 300°C .

10

In general terms, said polymer is preferably substantially stable when used as a PEM in a fuel cell. Thus, it suitably has high resistance to oxidation, reduction and hydrolysis and has very low permeability to
15 reactants in the fuel cell. Preferably, however, it has a high proton conductivity. Furthermore, it suitably has high mechanical strength and is capable of being bonded to other components which make up a membrane electrode assembly.

20

Said polymer may comprise a film, suitably having a thickness of less than 1mm , preferably less than 0.5mm , more preferably less than 0.1mm , especially less than 0.05mm . The film may have a thickness of at least $5\mu\text{m}$.

25

Said polymer electrolyte membrane may comprise one or more layers wherein, suitably, at least one layer comprises a film of said polymer. Said membrane may have a thickness of at least $5\mu\text{m}$ and, suitably, less than 1mm , preferably
30 less than 0.5mm , more preferably less than 0.1mm , especially less than 0.05mm .

The polymer electrolyte membrane may be a composite membrane which suitably includes a support material for the conductive polymer for importing mechanical strength and dimensional stability to the membrane. The polymer may be associated with the support material to form a composite membrane in a variety of ways. For example, an unsupported conductive polymer film can be preformed and laminated to the support material. Alternatively, (and preferably) the support material may be porous and a solution of the conductive polymer can be impregnated into the support material. In one embodiment, the support material may comprise, or preferably consist essentially of, polytetrafluoroethylene, suitably provided as a porous film. Such a support material may be as described and used in accordance with the teachings of WO97/25369 and WO96/28242, the contents of which are incorporated herein by reference. Suitably, the support material has a porous microstructure of polymeric fibrils and is impregnated with said polymer throughout the material, preferably so as to render an interior volume of the membrane substantially occlusive.

The use of support material as described may allow polymers of lower equivalent weights (EW) (for example less than 500 g/mol, less than 450 g/mol or even less than 400 g/mol or 370 g/mol) or relatively inflexible and/or brittle polymers to be used in polymer electrolyte membranes.

The polymer electrolyte membrane suitably includes a layer of a catalyst material, which may be a platinum catalyst (i.e. platinum containing) or a mixture of platinum and ruthenium, on both sides of the polymer film. Electrodes may be provided outside the catalyst material.

It may be preferable for each phenyl group in a sulphonated polymer as described to be deactivated by being bonded directly to an electron withdrawing group, for example a sulphonated group, a sulphone group or a ketone group.

According to a second aspect of the invention, there is provided a polymer electrolyte membrane which includes a polymer which includes: polyaryletherketone and/or polyarylethersulphone units; and units of formula $-O-Ph_n-O-$ (XX) wherein Ph represents a phenyl group and n represents an integer of 2 or greater and wherein Ph groups of units (XX) are sulphonated.

Preferably, each phenyl group of moiety Ph_n is sulphonated, preferably mono-sulphonated. About 100 mole% of such phenyl groups may be sulphonated as described.

Preferably, $-OPhCO-$ and/or $-OPhSO_2-$ moieties of said polymer are sulphonated to a lesser extent than the phenyl groups of moiety Ph_n . Moieties $-OPhCO-$ and $-OPhSO_2-$ may be substantially non-sulphonated.

In one embodiment, said polymer may include no ketone linkages and may have an equivalent weight of more than 900. Nonetheless, it has been found, surprisingly, that such polymers are still conducting.

Said polymer electrolyte membrane may be for a fuel cell or an electrolyser.

The invention extends to the use of a polymer which includes relatively easy to sulphonate units and relatively difficult to sulphonate units in the preparation of a polymer for a polymer electrolyte membrane.

5

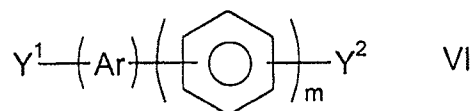
The polymer electrolyte membrane described herein may include a blend of polymers, at least one of which is a polymer described according to the invention described herein. Suitably the polymers described herein are blended
10 with 0-40wt%, preferably 0-20wt%, more preferably 0-10wt%, especially 0-5wt% of other polymeric material. Preferably, however, a blend of polymers is not provided.

According to a third aspect of the invention, there is
15 provided a fuel cell or an electrolyser (especially a fuel cell) incorporating a polymer electrolyte membrane according to the first or second aspects.

According to a fourth aspect of the invention, there is
20 provided any novel polymer as described according to said first aspect per se.

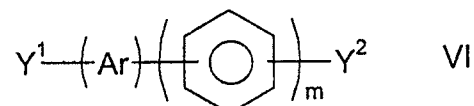
According to a fifth aspect of the invention, there is provided a process for the preparation of a polymer as
25 described in the first, second, third and/or fourth aspects, the process comprising:

(a) polycondensing a compound of general formula

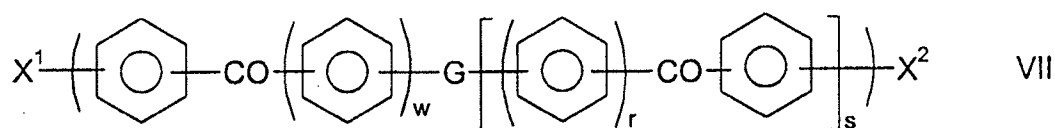


with itself wherein Y^1 represents a halogen atom or a group $-EH$ and Y^2 represents a halogen atom or, if Y^1 represents a halogen atom, Y^2 represents a group $E'H$; or

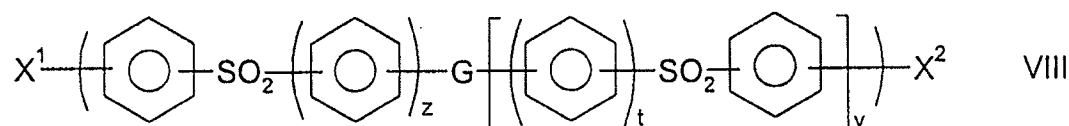
5 (b) polycondensing a compound of general formula



10 with a compound of formula



and/or with a compound of formula



15

wherein Y^1 represents a halogen atom or a group $-EH$ (or $-E'H$ if appropriate) and X^1 represents the other one of a halogen atom or group $-EH$ (or $-E'H$ if appropriate) and Y^2 represents a halogen atom or a group $-E'H$ and X^2 represents the other one of a halogen atom or a group $-E'H$ (or $-EH$ if appropriate).

20

(c) optionally copolymerizing a product of a process as described in paragraph (a) with a product of a process as described in paragraph (b);

5 wherein the phenyl moieties of units VI, VII and/or VIII are optionally substituted; the compounds VI, VII and/or VIII are optionally sulphonated; and Ar, m, w, r, s, z, t, v, G, E and E' are as described above except that E and E' do not represent a direct link;

10

the process also optionally comprising sulphonating and/or cross-linking a product of the reaction described in paragraphs (a), (b) and/or (c) to prepare said polymer.

15 In some situations, the polymer prepared, more particularly phenyl groups thereof, may be optionally substituted with the groups hereinabove described after polymer formation.

20 Preferably, where Y^1 , Y^2 , X^1 and/or X^2 represent a halogen, especially a fluorine, atom, an activating group, especially a carbonyl or sulphone group, is arranged ortho- or para- to the halogen atom.

25 Advantageously, where it is desired to prepare a copolymer comprising a first repeat unit IV or V wherein E represent an oxygen or sulphur atom, Ar represents a moiety of structure (i), m represents zero, E' represents a direct link, A represents 1 and B represents zero and a second
30 repeat unit IV or V wherein E and E' represent an oxygen or sulphur atom, Ar represents a moiety of structure (iv), m and w represent 1, G represents a direct link, s represents zero and A and B represent 1 wherein the polymer is not a

random polymer but has a regular structure, the process described in paragraph (b) above may be used wherein in said compound of general formula VI, Y^1 and Y^2 represent -OH or -SH groups, Ar represents a moiety of structure (iv) and m represents 1 and in said compounds of general formulae VII and VIII, X^1 and X^2 represent a fluorine atom, w,r,s,z,t and v represent 1 and G represents an oxygen or sulphur atom.

10 In another embodiment, where it is desired to prepare a copolymer comprising a first repeat unit IV or V wherein E and E' represent an oxygen or sulphur atom, Ar represents a moiety of structure (iv), m represents zero, A represents 1, w represents 1, s represents zero and B represents 1 and
15 a second repeat unit IV or V wherein E and E' represent an oxygen or sulphur atom, Ar represents a moiety of structure (iv), m and w represent 1, s represents zero and A and B represent 1, wherein the polymer is not a random polymer but has a regular structure, the process described in
20 paragraph (b) above may be used wherein in said compound of general formula VI, Y^1 and Y^2 represent -OH or -SH groups, Ar represents a moiety of structure (iv) and m represents 1 and in said compounds of general formulae VII and VIII, X^1 and X^2 represent a fluorine atom, w,r,s,z,t and v represent
25 1 and G represents a -O-Ph-O- moiety.

Preferred halogen atoms are fluorine and chlorine atoms, with fluorine atoms being especially preferred. Preferably, halogen atoms are arranged meta- or para- to
30 activating groups, especially carbonyl groups.

Where the process described in paragraph (a) is carried out, preferably one of Y^1 and Y^2 represents a fluorine atom

and the other represents an hydroxy group. More preferably in this case, Y^1 represents a fluorine atom and Y^2 represents an hydroxy group. Advantageously, the process described in paragraph (a) may be used when Ar represents a moiety of structure (i) and m represents 1.

When a process described in paragraph (b) is carried out, preferably, Y^1 and Y^2 each represent an hydroxy group. Preferably, X^1 and X^2 each represent a halogen atom, suitably the same halogen atom.

Compounds of general formula VI, VII and VIII are commercially available (eg from Aldrich U.K.) and/or may be prepared by standard techniques, generally involving Friedel-Crafts reactions, followed by appropriate derivatisation of functional groups. The preparations of some of the monomers described herein are described in P M Hergenrother, B J Jensen and S J Havens, Polymer 29, 358 (1988), H R Kricheldorf and U Delius, Macromolecules 22, 517 (1989) and P A Staniland, Bull, Soc, Chem, Belg., 98 (9-10), 667 (1989).

Where compounds VI, VII and/or VIII are sulphonated, compounds of formulas VI, VII and/or VIII which are not sulphonated may be prepared and such compounds may be sulphonated prior to said polycondensation reaction.

Sulphonation as described herein may be carried out in concentrated sulphuric acid (suitably at least 96% w/w, preferably at least 97%w/w, more preferably at least 98%w/w; and preferably less than 98.5%w/w) at an elevated temperature. For example, dried polymer may be contacted with sulphuric acid and heated with stirring at a

temperature of greater than 40°C, preferably greater than 55°C, for at least one hour, preferably at least two hours, more preferably about three hours. The desired product may be caused to precipitate, suitably by contact with cooled
5 water, and isolated by standard techniques. Sulphonation may also be effected as described in US5362836 and/or EP0041780.

Where the process described in paragraph (b) is carried
10 out, suitably, "a*" represents the mole% of compound VI used in the process; "b*" represents the mole % of compound VII used in the process; and "c*" represents the mole % of compound VIII used in the process.

15 Preferably, a* is in the range 45-55, especially in the range 48-52. Preferably, the sum of b* and c* is in the range 45-55, especially in the range 48-52. Preferably, the sum of a*, b* and c* is 100.

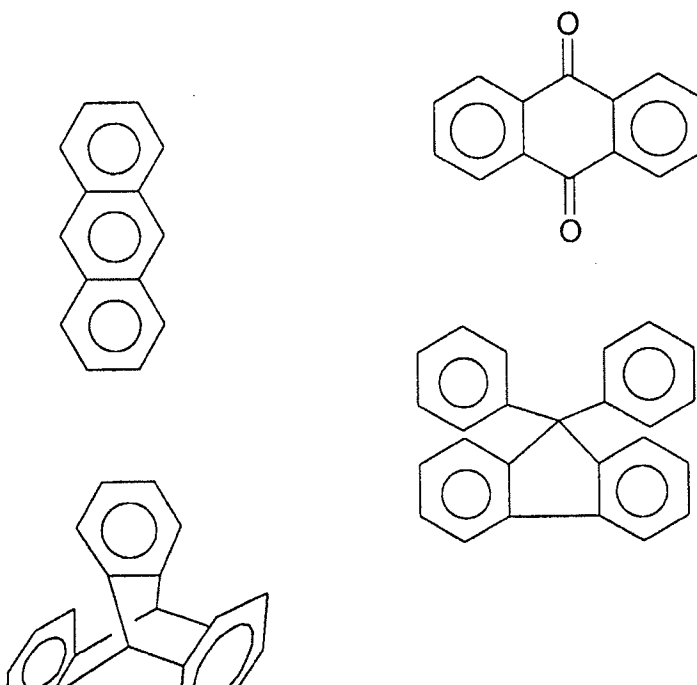
20 Where the process described in paragraph (b) is carried out, preferably, one of either the total mole % of halogen atoms or groups -EH/-E'H in compounds VI, VII and VIII is greater, for example by up to 10%, especially up to 5%, than the total mole % of the other one of either the total
25 mole % of halogen atoms or groups -EH/-E'H in compounds VI, VII and VIII. Where the mole % of halogen atoms is greater, the polymer may have halogen end groups and be more stable than when the mole % of groups -EH/-E'H is greater in which case the polymer will have -EH/-E'H end groups. However,
30 polymers having -EH/-E'H end groups may be advantageously cross-linked.

The molecular weight of the polymer can also be controlled by using an excess of halogen or hydroxy reactants. The excess may typically be in the range 0.1 to 5.0 mole %. The polymerisation reaction may be terminated
5 by addition of one or more monofunctional reactants as end-cappers.

It is believed that certain polymers described herein are novel and, therefore, in a sixth aspect, the invention
10 extends to any novel polymer described herein per se.

It is also believed that certain polymers according to said first and/or second aspect but which are not sulphonated are novel. Thus, according to a seventh aspect
15 of the invention, there is provided a novel polymer having a moiety of formula I and/or a moiety of formula II and/or a moiety of formula III wherein E, E', G, m, r, s, t, v, w, z and Ar are as described in any statement herein.

20 Preferably, said polymer includes a moiety of formula II and/or III and Ar is selected from



Preferably, in the aforementioned formulae, each -Ar- is bonded to adjacent moieties as described in any statement herein.

5

According to an eighth aspect of the invention, there is provided a process for the preparation of novel polymers according to said seventh aspect, the process being as described according to the process of the fifth aspect
10 except that compounds VI, VII and VIII are not sulphonated and the process does not include a sulphonation step.

Sulphonated polymers described herein may be made into films and/or membranes for use as PEMs by conventional
15 techniques, for example as described in Examples 5 to 7 of US 5561202.

The sulphonated polymers described herein may be used as polymer electrolyte membranes in fuel cells or
20 electrolyzers as described. Additionally, they may be used in gas diffusion electrodes.

Any feature of any aspect of any invention or example described herein may be combined with any feature of any
25 aspect of any other invention or example described herein.

Specific embodiments of the invention will now be described, by way of example, with reference to figure 1 which is a schematic representation of a polymer
30 electrolyte membrane fuel cell.

As described above, the fuel cell includes a thin sheet
2 of a hydrogen-ion conducting Polymer Electrolyte

Membrane. The preparation of sheet material for such a membrane is described hereinafter.

Example 1

5

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybenzophenone (34.28g, 0.16
10 mole), 4,4'-dihydroxybiphenyl (44.69g, 0.24 mole) and diphenylsulphone (332g) and purged with nitrogen for at least 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 145°C to form an almost colourless solution. While maintaining a nitrogen
15 blanket, dried sodium carbonate (43.24g, 0.408 mole) was added. The temperature was raised gradually to 335°C over 200 minutes then maintained for 1 hour.

The reaction mixture was allowed to cool, milled and
20 washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a Tg of 164°C, a melt viscosity at 400°C, 1000sec⁻¹ of 0.48 kNsm⁻² and an inherent viscosity (IV) 0.40 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of
25 density 1.84g.cm⁻³, said solution containing 0.1g of polymer/100cm³).

Examples 2 to 6

30 The polymerisation procedure of Example 1 was followed, except that copolymers of different compositions were prepared by varying the mole ratios of 4,4'-dihydroxybenzophenone to 4,4'-dihydroxybiphenyl, with the

sum of the number of moles of the aforesaid reactants
equalling the number of moles of 4,4'-
difluorobenzophenone, as described in Example 1. A
summary of the mole ratios and the MV are detailed in the
5 table below.

| Example No | 4,4' dihydroxybiphenyl: 4,4' - dihydroxybenzophenone | MV (kNsm ⁻²) |
|------------|--|--------------------------|
| 2 | 2:1 | 0.17 |
| 3a | 1:1 | 0.48 |
| 3b* | 1:1 | 0.69 |
| 4 | 1:2 | 0.54 |
| 5 | 1:3 | 0.43 |
| 6 | 1.25:1 | 0.34 |

* The polymerisation procedure of Example 1 was followed except dried sodium carbonate (43.24g, 0.408 mole) was replaced by dried sodium carbonate (42.44g, 0.4 mole) and dried potassium carbonate (1.11g, 0.008 mole).

Example 7a

10 A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (37.24g, 0.2 mole) 4,4'-dihydroxydiphenylsulphone (50.05g, 0.2 mole), and
15 diphenylsulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (42.44g, 0.4 mole) and
20 potassium carbonate (1.11g, 0.008 mole) were added. The temperature was raised gradually to 315°C over 3 hours then maintained for 0.5 hours.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a Tg of 183°C, a melt viscosity at 400°C, 1000sec⁻¹ of 0.78 kNsm⁻² and an inherent viscosity (IV) 0.40 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm⁻³, the solution containing 0.1g of polymer/100cm³).

10 Example 7b

The polymerisation procedure of Example 7a was followed except dried sodium carbonate (42.44g, 0.4 mole) and dried potassium carbonate (1.11g, 0.008 mole) was replaced by dried sodium carbonate only (43.24g, 0.408 mole). The polymer had a Tg of 183°C and a melt viscosity at 400°C, 1000sec⁻¹ of 0.43 kNsm⁻²

Examples 8 and 10

20

The polymerisation procedure of Example 7b was followed, except that copolymers were prepared by varying the mole ratios of the hydroxy-containing reactants, with the sum of the number of moles of the aforesaid equalling the number of moles of 4,4'-difluorobenzophenone. A summary of the mole ratios and the MV are detailed in the table below.

| Example No | 4,4'-dihydroxybiphenyl : 4,4'-dihydroxydiphenyl-sulphone | MV (kNsm ⁻²) |
|------------|--|--------------------------|
| 8 | 1:2 | 0.67 |
| 9 | 1:3 | 0.72 |
| 10 | 1:1.5 | 0.6 |

Example 11

A 700ml flanged flask fitted with a ground glass
5 Quickfit lid, stirrer/stirrer guide, nitrogen inlet and
outlet was charged with 4,4'-dichlorodiphenylsulphone
(104.25g, 0.36 mole), 4,4'-dihydroxydiphenylsulphone
(6.75g, 0.27 mole), 4,4'-dihydroxybiphenyl (16.74g, 0.09
10 mole) and diphenylsulphone (245g) and purged with nitrogen
for at least 1 hour. The contents were then heated under
a nitrogen blanket to between 140 and 145°C to form an
almost colourless solution. While maintaining a nitrogen
blanket potassium carbonates (50.76g, 0.37 mole) was
added. The temperature was raised to 180°C, held for 0.5
15 hours, raised to 205°C, held for 1 hour, raised to 225°C,
held for 2 hours, raised to 265°C, held for 0.5 hours,
raised to 280°C and held for 2 hours.

The reaction mixture was allowed to cool, milled and
20 washed with acetone/methanol (30/70) and water. The
resulting polymer was dried in an air oven at 120°C.

Example 12

25

The polymerisation procedure of Example 11 was
followed, except that the ratio of 4,4'-dihydroxybiphenyl
to 4,4'-dihydroxydiphenylsulphone was 1:2. The polymer
has a Tg of 198°C and on RV of 0.52.

30

Example 13 - Sulphonation of Polymers of Examples 1 to12

The polymers of Examples 1 to 12 were sulphonated by stirring each polymer in 98% sulphuric acid (3.84g polymer/100g sulphuric acid) for 21 hours at 50°C. Thereafter, the reaction solution was allowed to drip into stirred deionised water. Sulphonated polymer precipitated as free-flowing beads. Recovery was by filtration, followed by washing with deionised water until the pH was neutral and subsequent drying. In general, ¹H nmr in DMSO-d₆ confirmed that 100 mole% of the biphenyl units had sulphonated, giving one sulphonic acid group, ortho to the ether linkage, on each of the two aromatic rings comprising the biphenyl unit. For examples 3 to 5, 100% sulphonation of -O-Ph-Ph-O- moieties was confirmed by converting the sulphonated ionomer from the H⁺ form to Na⁺ form, by reacting 0.5g of the dry sulphonated copolymer with an aqueous solution of NaOH (2.5g NaOH/200ml water) at 60-65°C for 2 hours then washing the product with water and drying at 60°C, followed by sodium analysis.

Example 14 - Membrane Fabrication

Membranes were produced from selected polymers of Examples 1 to 12 after sulphonation as described in Example 13 by dissolving respective polymers in N-methylpyrrolidone (NMP). The polymers were dissolved at a concentration of 15% wt/v, except for Examples 3a and 6 which were dissolved to 4% wt/v. The homogeneous solutions were cast onto clean glass plates and then drawn down to give 300 micron films, using a stainless steel Gardner Knife. Evaporation at 100°C under vacuum for 24

hours produced membranes of mean thickness 40 microns except that Examples 3a and 6 produced membranes of about 10 microns.

5 Example 15 - Water-uptake of the Membranes

5cm x 5cm x 40 microns samples of membranes of Example 14 were immersed in deionized water (500ml) for 3 days, dried quickly with lint-free paper to remove surface water
10 and weighed, dried in an oven at 50°C for 1 day, allowed to cool to ambient temperature in a desiccator then weighed quickly.

The water uptake was measured as follows, with the
15 results being provided in the table below. "Equivalent weight" is defined as the weight of polymer containing unit weight of replaceable acidic hydrogen.

$$\% \text{ Water Up-take} = \frac{\text{Wet Weight} - \text{Dry Weight}}{\text{Dry Weight}} \times 100$$

20

Dry Weight

| Membrane - prepared from sulphonated polymer of Example No: | Equivalent Weight (g/mol) | % Water Up-take |
|--|------------------------------|-----------------|
| 2 | 360 | 136.4 |
| 3a | 458 | 54.4 |
| 6 | 419 | 69.3 |
| 7a | 476 | 61.5 |
| 8 | 690 | 30.5 |
| 9 | 904 | 21.9 |
| 10 | 583 | 38.7 |
| 11 | 976 | 21.6 |
| 12 | 744 | 30.7 |

Example 16 - Performance of membranes in a Polymer Electrolyte Membrane Fuel Cell

The membranes prepared from sulphonated polymers of Examples 8 to 11 were installed in a Standard PEMFC single cell test module and polarisation data was generated and compared to Nafion 115, a leading commercially-available membrane. The current densities obtained at 0.8V were 0.42, 0.35, 0.58 and 0.26 Acm⁻² for the Example 8 to 11 polymers respectively, compared to 0.12 Acm⁻² for Nafion 115.

Example 17

The S number of a polymer is defined as follows:

$$\text{S Number} = \frac{\text{Number of unsulphonated phenyls}}{\text{Number of sulphonated phenyls}}$$

The S number for polymers described above is summarised in the table below.

| Example No. | S Number |
|-------------|----------|
| 1 | 2.33 |
| 2 | 2 |
| 3 | 3 |
| 4 | 5 |
| 5 | 7 |
| 6 | 2.6 |
| 7a | 3 |
| 8 | 5 |
| 9 | 7 |
| 10 | 4 |

| | |
|----|---|
| 11 | 7 |
| 12 | 5 |

Example 18

A 500ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-difluorobenzophenone (35.79g, 0.164 mole), hydroquinone (11.01g, 0.10 mole), 4,4'-dihydroxybiphenyl (18.62g, 0.10 mole), 4,4'-bis(4-chlorophenylsulphonyl)biphenyl (LCDC) (20.13g, 0.04 mole) and diphenylsulphone (202.76g) and the contents were heated under a nitrogen blanket to 160°C to form a nearly colourless solution. While maintaining a nitrogen blanket, anhydrous potassium carbonate (29.02g, 0.21 mole) was added and the mixture stirred for 35 minutes. The temperature was raised gradually to 220°C over 2 hours then raised to 280°C over 2 hours and maintained for 2 hours.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer had a reduced viscosity of (RV) 2.50 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm⁻³, said solution containing 1g of polymer/100cm³) and a Tg of 186°C.

Example 19

A 250ml, 3-necked round-bottomed flask fitted with stirrer, nitrogen inlet and air condenser was charged with 4,4'-difluorobenzophenone (33.06g, 0.1515 mole),

hydroquinone (13.21g, 0.12 mole), 9,9'-bis(4-hydroxyphenyl)fluorene (HPF) (10.512g, 0.03 mole), and diphenylsulphone (100.93g) and the contents were heated under a nitrogen blanket to 150°C to form a nearly
5 colourless solution. While maintaining a nitrogen blanket, anhydrous potassium carbonate (21.77g, 0.15751 mole) was added. The temperature was raised to 175°C maintained for 2 hours, raised to 200°C maintained for 50 minutes, raised to 250°C maintained for 45 minutes, raised to 300°C
10 maintained for 90 minutes.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer
15 had an reduced viscosity (RV) of 0.76 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm⁻³, said solution containing 1g of polymer/100cm³) and a Tg of 165°C.

20 n Example 20

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-bis(4-chlorophenylsulphonyl)-terphenyl (23.2g, 0.04
25 mole), 4,4'-dihydroxybiphenyl (7.44g, 0.040 mole) and diphenylsulphone (80g) and the contents were heated under a nitrogen blanket to 170°C to form a nearly colourless solution. While maintaining a nitrogen blanket, anhydrous potassium carbonate (5.64g, 0.408 mole) was added. The
30 temperature was raised to 200°C and maintained for 30 minutes, raised to 250°C and maintained for 15 minutes, raised to 275°C and maintained for 15 minutes, raised to 330°C and maintained for 1 hour.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer
5 had an inherent viscosity (IV) of 0.50 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm⁻³, said solution containing 0.1g of polymer/100cm³) and a Tg of 264°C.

10 Example 21

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-difluorobenzophenone (21.82g, 0.10 mole), 4,4'-
15 dihydroxybiphenyl (18.62g, 0.10 mole) and diphenylsulphone (60g) and the contents were heated under a nitrogen blanket to 180°C to form a nearly colourless solution. While maintaining a nitrogen blanket anhydrous potassium carbonate (14.10g, 0.102 mole) was added. The temperature
20 was raised to 200°C over 60 minutes, raised to 250°C maintained for 5 mins, raised to 325°C maintained for 5 mins, raised to 370°C over 90 mins, maintained for 10 mins.

The reaction mixture was allowed to cool, milled and
25 washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer had an inherent viscosity (RV) of 1.28 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm⁻³, said solution containing 1g of
30 polymer/100cm³) and a Tg 167°C.

Example 22

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-difluorobenzophenone (22.04g, 0.101 mole), 4,4'-dihydroxybiphenyl (6.52g, 0.035 mole), hydroquinone (7.16g, 0.065 mole) and diphenylsulphone (60g) and the contents were heated under a nitrogen blanket to 180°C to form a nearly colourless solution. While maintaining a nitrogen blanket anhydrous sodium carbonate (10.60g, 0.100 mole) and anhydrous potassium carbonate (0.28g, 0.002 mole) were added. The temperature was raised to 200°C held for 1 hour, raised to 250°C held for 1 hour, raised to 300°C held for 1 hour. The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer has an inherent viscosity (IV) 0.92 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84 g.cm⁻³, said solution containing 0.1 g of polymer/100cm³) and a Tg 156°C.

20 Example 23

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-bis(4-fluorobenzoyl)diphenylether (21.34g, 0.515 mole), 4,4'-dihydroxybiphenyl (9.31g, 0.050 mole) and diphenylsulphone (90g) and the contents were heated under a nitrogen blanket to 160°C to form a nearly colourless solution. While maintaining a nitrogen blanket anhydrous sodium carbonate (5.30g, 0.050 mole) and anhydrous potassium carbonate (0.14g, 0.001 mole) were added. The temperature was raised at 1°C/min until it reached 345°C and held for 1 hour.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer had an inherent viscosity (RV) 1.48 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm⁻³, said solution containing 1g of polymer/100cm³) and a Tg 163°C.

Example 24 - General procedure for Sulphonation of Polymers of Examples 18 to 23

The polymers prepared as described in Examples 18 to 23 were sulphonated according to the following procedure.

The dried polymer was placed in a three-necked round-bottomed flask fitted with a stirrer containing 98% concentrated sulphuric acid (100cm³), heated with stirring to 60°C and maintained at the temperature for 3 hours. The reaction product was poured into 5 litres of stirred ice/water mixture. The product precipitated out. It was then filtered-off, washed with iced-water until the pH was neutral, washed with methanol and dried under vacuum at 100°C. The degree of sulphonation was determined by elemental analysis, filtration or Nmr.

Example 25 - Sulphonation of polymer of Example 22

The dried polymer from Example 22(10g) was placed in a three-necked round-bottomed flask fitted with a stirrer, containing 98% concentrated sulphuric acid (100cm³), heated

with stirring to 60°C and maintained at that temperature for 3 hours. The reaction products was poured into 5 litres of stirred ice/water mixture. The product precipitated out, was filtered-off, washed with iced-water until the pH was neutral, washed with methanol and dried under vacuum at 100°C. Nmr analysis showed the polymer had readily sulphonated, in which 95-100 mole% of the ether-diphenyl-ether and ether-phenyl-ether units had been sulphonated.

10

Example 26

A 500ml 3-necked round bottomed quickfit flask fitted with stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (22.04g, 0.102 mole), 4,4'-dihydroxybenzophenone (10.71g, 0.05 mole), 2,7-dihydroxynaphthalene (8.01g, 0.05 mole) and diphenyl sulphone (76.9g) and purged with nitrogen for at least 1 hour. The contents were heated under a nitrogen blanket to about 132°C to form a clear solution. While maintaining a nitrogen blanket, dried sodium carbonate (10.81g, 0.102 mole) was added. The temperature was raised gradually to 290°C over 240 minutes then maintained for 65 minutes.

25

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer had a Tg of 158°C and melt viscosity at 400°C, 1000sec⁻¹ of 0.5 kNsm⁻².

30

The polymer was sulphonated using the process described in Example 13. The resultant sulphonated

polymer has a water-uptake of 69.3% and an equivalent weight of 445.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

10

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

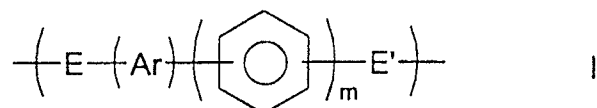
Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

25

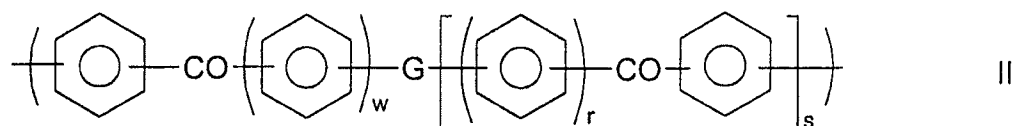
The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

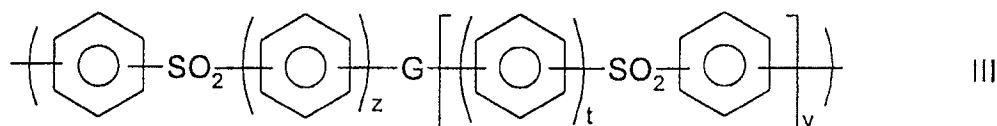
1. A polymer electrolyte membrane which includes a
 5 polymer having a moiety of formula



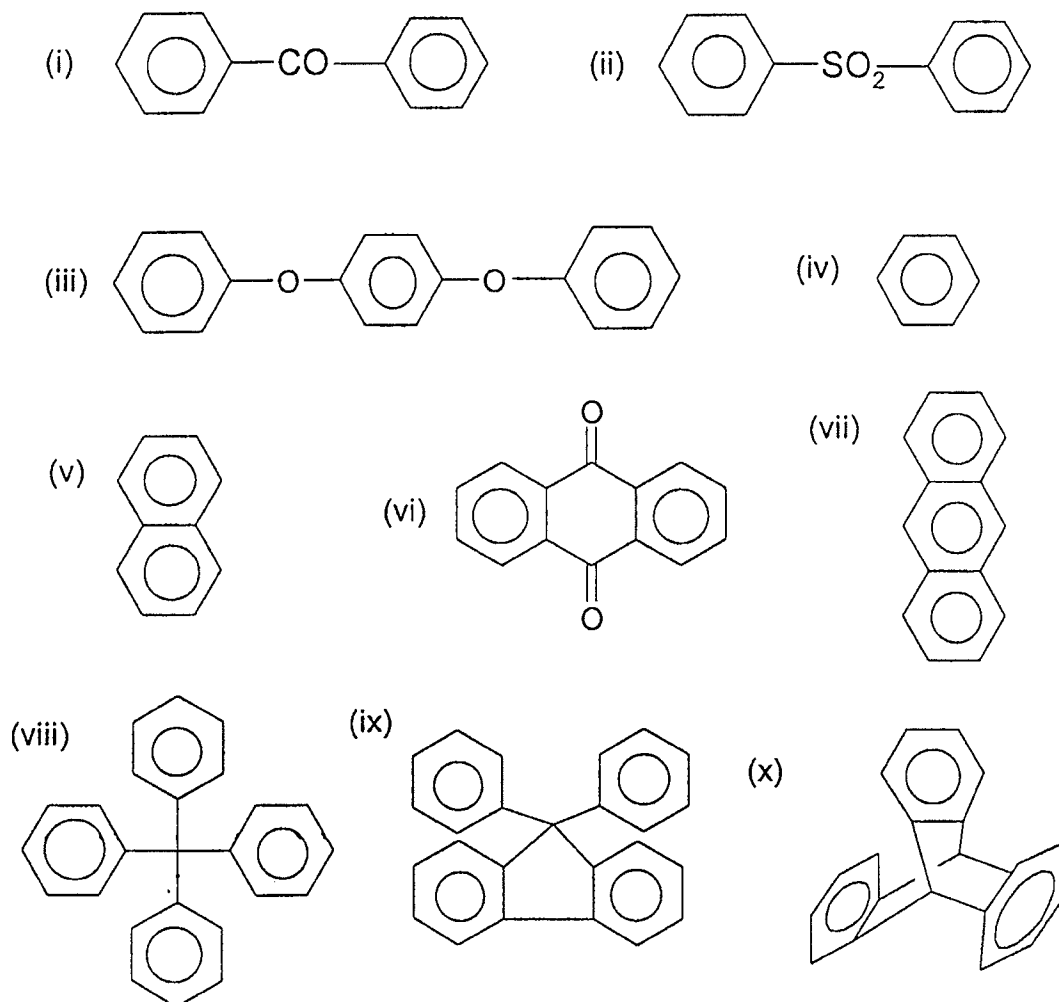
and/or a moiety of formula



- 10 and/or a moiety of formula



- wherein at least some of the units I, II, and/or III
 are sulphonated; wherein the phenyl moieties in units I,
 II and III are independently optionally substituted and
 15 optionally cross-linked; and wherein m, r, s, t, v, w and z
 independently represent zero or a positive integer, E and
 E' independently represent an oxygen or a sulphur atom or
 a direct link, G represents an oxygen or a sulphur atom, a
 direct link or a -O-Ph-O- moiety where Ph represents a
 20 phenyl group and Ar is selected from one of the following
 moieties (i) to (x) which is bonded via one or more of its
 phenyl moieties to adjacent moieties



2. A polymer electrolyte membrane which includes a polymer having a moiety of formula I and/or a moiety of formula II and/or a moiety of formula III as described in claim 1, wherein at least some of units I, II and/or III are functionalized to provide ion exchange sites.

3. A membrane according to claim 1 or claim 2, wherein said polymer is crystalline.

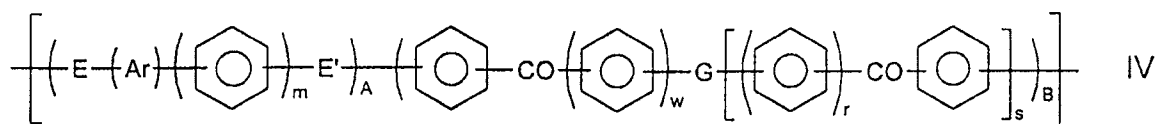
4. A membrane according to any preceding claim, wherein "a" represents the mole % of units of formula I in said

polymer; "b" represents the mole % of units of formula II in said polymer; and "c" represents the mole % of units of formula III in said polymer and wherein a is in the range 45-100 and the sum of b and c is in the range of 0-55.

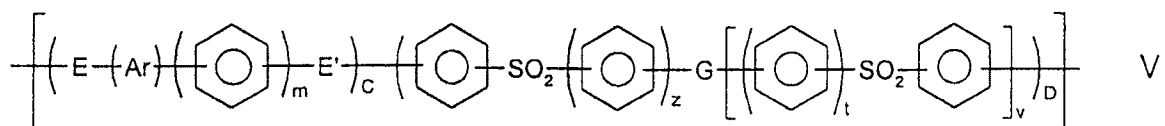
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5. A membrane according to any preceding claim, wherein said polymer consists essentially of moieties I, II and/or III.

10 6. A membrane according to any preceding claim, wherein said polymer is a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general
15 formula



or a random or block copolymer of at least two different units of IV and/or V

20 wherein A, B, C and D independently represent 0 or 1.

7. A membrane according to claim 6, wherein said polymer includes at least one repeat unit of formula IV.

25 8. A membrane according to claim 6, wherein said polymer is a copolymer comprising a first repeat unit of formula

IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1; and

5

a second repeat unit of formula V wherein E and E' represent oxygen atoms, Ar represents a structure (i), m represents 0, C represents 1, z represents 1, G represents a direct link, v represents 0 and D represents 1.

10

9. A membrane according to claim 6, wherein said polymer is a copolymer comprising a first repeat unit of formula IV, wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents 0, A and B represent 1.

10. A membrane according to claim 6, wherein said polymer is a copolymer comprising a first repeat unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents 0, A and B represent 1; and a second repeat unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents 0.

11. A membrane according to claim 6, wherein said polymer is a copolymer comprising a first repeat unit which is either:

(a') of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a

moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1; or

(b') of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero;

and a second repeat unit which is either:

10

(c') of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1; or

15

(d') of formula IV wherein E represents an oxygen atom, E' is a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1, A and B represent 1.

20

12. A membrane according to claim 11, wherein said polymer has a repeat unit as described in paragraph (a') or (b') in combination with a repeat unit as described in paragraph (c').

25

13. A membrane according to claim 6, comprising a first repeat unit which is selected from the following:

(a) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1;

30

(b) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero;

5

(c) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1 and C and D represent 1;

10

(d) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; or

15

(e) a unit of formula V wherein E and E' represents an oxygen atom, Ar represents a structure (i), m represents 0, C represents 1, Z represents 1, G represents a direct link, v represents 0 and D represents 1;

20

and a second repeat unit which is selected from the following:

(f) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1;

25

(g) a unit of formula IV wherein E represents an oxygen atom, E' is a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represent 1, A and B represent 1;

30

(h) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, z represents 1, v represents 0, C and D represent 1; and

5

(i) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1, C and D represent 1;

10

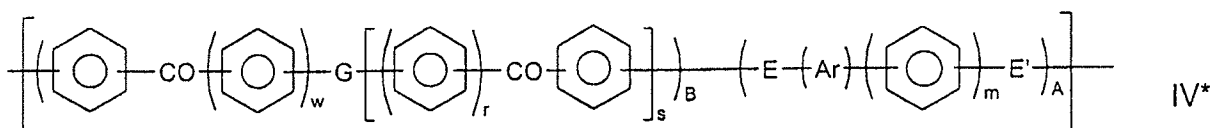
14. A membrane according to any of claims 6 to 13, wherein said second unit is selected from a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, w represents 1, s represents 0, A and B represent 1; or a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, z represents 1, v represents 0, c and d represent 1.

20

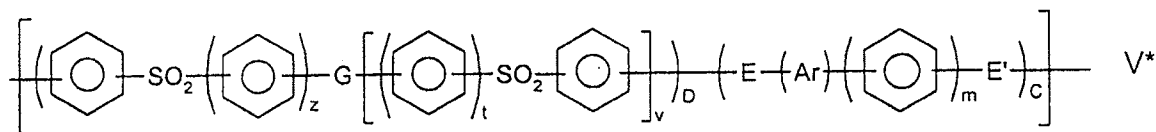
15. A membrane according to claim 13 or claim 14, wherein said copolymer has a first repeat unit selected from units (b), (d) or (e) in combination with a second repeat unit selected from units (f) or (h).

25

16. A membrane according to any of claims 1 to 5, wherein said polymer is a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general formula



5 or a random or block copolymer of at least two different units of IV* and/or V* wherein A, B, C and D independently represent 0 or 1.

17. A membrane according to claim 16, wherein said
 10 polymer includes: a repeat unit of formula IV* wherein E represents a direct link, E' represents an oxygen atom, G represents a direct link, w, s and m represent 0, A and B represent 1; and/or a repeat unit of formula V* wherein E represents a direct link, E' represents an oxygen atom, G
 15 represents a direct link, z, v and m represent 0, C and D represent 1.

18. A membrane according to claim 17 which includes a
 repeat unit of formula IV* or V* and any of units (a) to
 20 (i) according to claim 13.

19. A membrane according to any preceding claim, wherein
 said polymer includes at least some ketone moieties in the
 polymeric chain.

25

20. A membrane according to any preceding claim, wherein
 said polymer includes a biphenylene moiety.

21. A membrane according to any preceding claim, wherein said polymer includes a -O-biphenylene-O- moiety.

22. A membrane according to any preceding claim, wherein
5 said polymer includes a -O-naphthalene-O-moiety.

23. A membrane according to any preceding claim, wherein said polymer has a glass transition temperature (T_g) of at least 144°C.

10

24. A membrane according to claim 23, wherein said glass transition temperature is at least 154°C.

25. A membrane according to any preceding claim, wherein
15 said polymer has an inherent viscosity of at least 0.3.

26. A membrane according to any preceding claim, for a fuel cell.

20 27. A membrane according to any preceding claim, for an electrolyser.

28. A fuel cell incorporating a polymer electrolyte membrane according to any of claims 1 to 25..

25

29. An electrolyser incorporating a polymer electrolyte membrane according to any of claims 1 to 25.

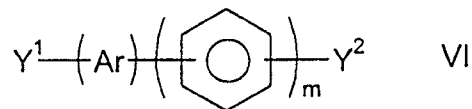
30. A gas diffusion electrode incorporating a polymer
30 electrolyte membrane according to any of claims 1 to 25.

31. A novel polymer as described in any of claims 1 to 25
per se.

32. A process for the preparation of a polymer as described in any of claims 1 to 25, the process comprising:

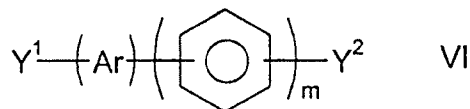
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(a) polycondensing a compound of general formula



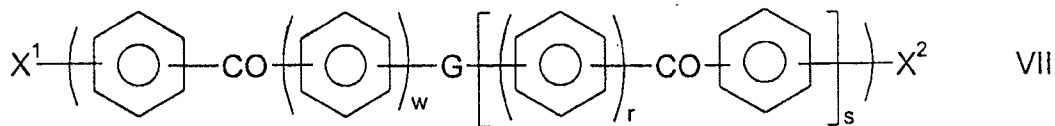
with itself wherein Y^1 represents a halogen atom or a
 10 group $-EH$ and Y^2 represents a halogen atom or, if Y^1
 represents a halogen atom, Y^2 represents a group $E'H$; or

(b) polycondensing a compound of general formula

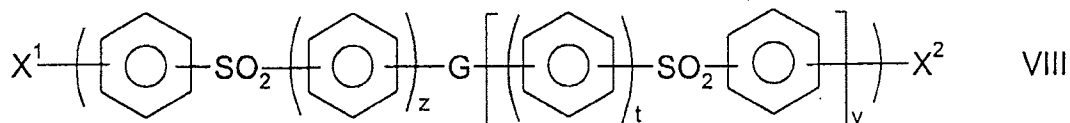


15

with a compound of formula



and/or with a compound of formula



wherein Y^1 represents a halogen atom or a group -EH
(or -E'H if appropriate) and Y^2 represents a halogen atom
or a group -E'H and X^2 represents the other one of a
5 halogen atom or a group -E'H (or EH of appropriate); and

(c) optionally copolymerizing a product of a process
as described in paragraph (a) with a product of a process
as described in paragraph (b);

10

wherein the phenyl moieties of units VI, VII and/or
VIII are optionally substituted; the compounds VI, VII
and/or VIII are optionally sulphonated; and Ar, m, w, r,
s, z, t, v, G, E and E' are as described in any of claims
15 1 to 20 except that E and E' do not represent a direct
link; the process also optionally comprising sulphonating
and/or cross-linking a product of the reaction described
in paragraphs (a), (b) and/or (c) to prepare said polymer.

20 33. A process according to claim 31, wherein sulphonation
is carried out in concentrated sulphuric acid at an
elevated temperature.

34. A novel polymer as described in any of claims 1 to 24
25 (except that the polymer is not sulphonated) *per se*.

35. A membrane, a fuel cell, a process, a novel polymer,
each being independently substantially as hereinbefore
described, with reference to the examples.

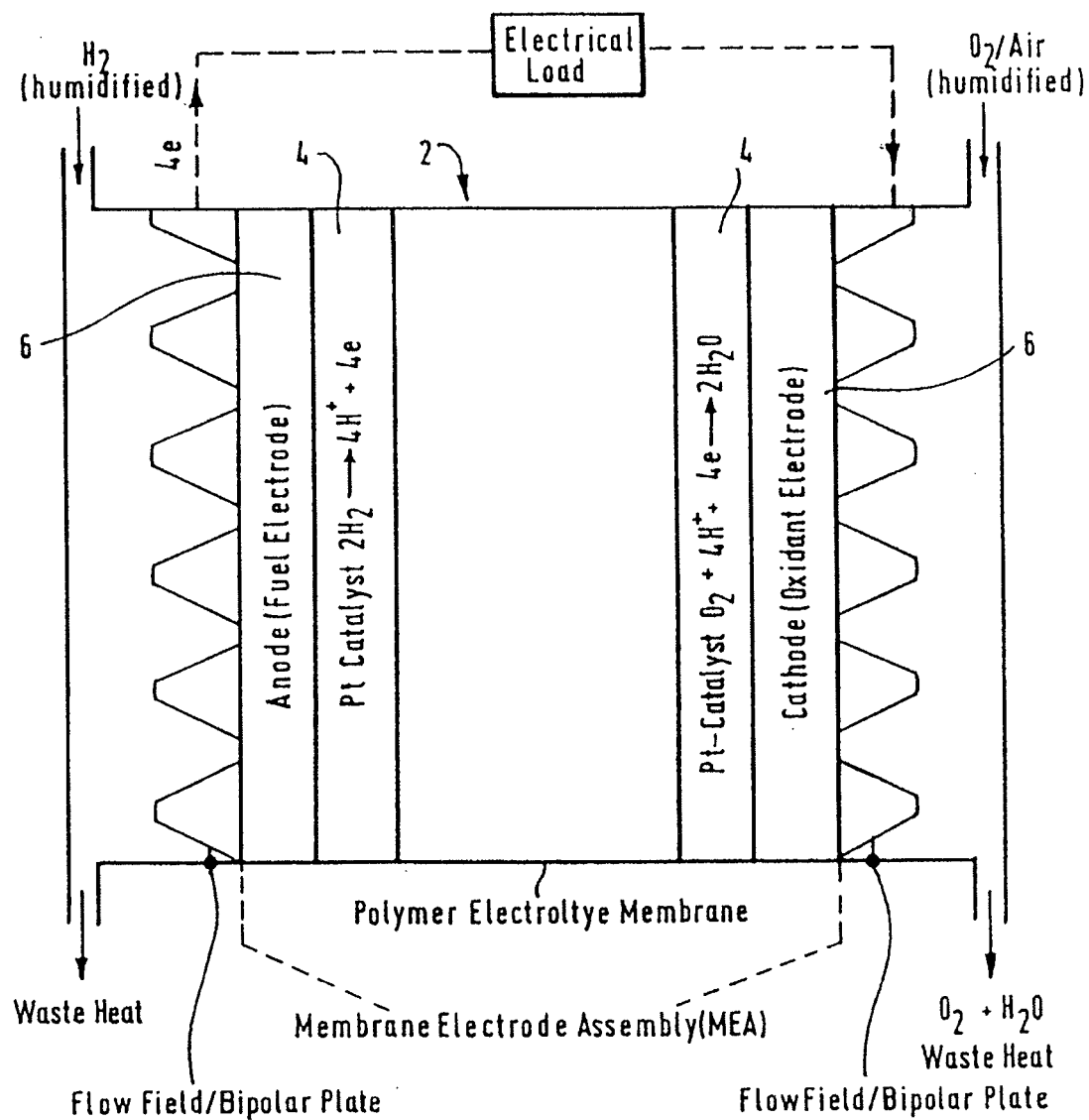


FIG.1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/02833

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G65/48 C08J5/22 H01M6/18 H01M10/40 H01M8/10
H01M2/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C08J H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|------------------------|
| X | EP 0 574 791 A (HOECHST AG) 22 December 1993 (1993-12-22) cited in the application claims 1-19 page 7, line 35 - line 45 --- | 1-35 |
| X | WO 96 29360 A (CLAUSS JOACHIM ;DECKERS GREGOR (DE); HOECHST AG (DE); WITTELER HEL) 26 September 1996 (1996-09-26) cited in the application claims 1-30 *Structure (III)* page 7 --- | 1-35 |
| X | EP 0 382 440 A (ICI PLC) 16 August 1990 (1990-08-16) claims 1,2 --- | 1-7, 16, 19, 34, 35 |
| | -/-- | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

3 December 1999

Date of mailing of the international search report

17. 01. 2000

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O'Sullivan, T

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02833

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| X | FR 2 748 485 A (COMMISSARIAT ENERGIE ATOMIQUE) 14 November 1997 (1997-11-14) claim 1; example 1 page 16, line 1 - line 6 --- | 1-3, 19-31 |
| X | EP 0 008 895 A (ICI PLC) 19 March 1980 (1980-03-19) cited in the application claim 1 example 1 page 4, line 22 - line 30 --- | 32,33 |
| X | EP 0 211 693 A (UNION CARBIDE CORP) 25 February 1987 (1987-02-25) column 11 -column 14 --- | 32-34 |
| P,X | EP 0 932 213 A (SUMITOMO CHEMICAL CO) 28 July 1999 (1999-07-28) claims 1,3 ----- | 1-35 |

INTERNATIONAL SEARCH REPORT

International Application No. PCT/GB 99/02833

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-35 (all in part)

Present claims 1-35 relate to an extremely large number of possible polymer types. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the polymers claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the polyarylether ketones or polyarylether sulphones described in the examples of the present application.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT, GB 99/02833

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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